

### **Patent Claims**

1. Sample holder for application in MALDI mass spectrometry, comprising:
  - a substrate
  - a porous film present on the substrate and comprising metal oxide particles.
2. Sample holder according to Claim 1, characterised in that the metal oxide particles are selected from the group including titanium dioxide, zirconium dioxide, niobium oxide, aluminium titanium oxide, tungsten zirconium oxide, hafnium dioxides, tungsten oxide, tin dioxide, lead oxide, lead dioxide, germanium dioxide and gallium oxide ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{NbO}$ ,  $\text{Al}_2\text{TiO}_5$ ,  $\text{W}_2\text{ZrO}_8$ ,  $\text{TiZrO}_4$ ,  $\text{HfO}_2$ ,  $\text{WO}_3$ ,  $\text{SnO}_2$ ,  $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{GeO}_2$  and  $\text{Ga}_2\text{O}_3$ ).
3. Sample holder according to any of the Claims 1 to 2, characterised in that the film has a mean pore size of  $< 50 \text{ nm}$ .
4. Sample holder according to Claim 3, characterised in that the film has a mean pore size in the range from  $1 \text{ nm}$  to  $25 \text{ nm}$ .
5. Sample holder according to Claim 4, characterised in that the film has a mean pore size in the range from  $1 \text{ nm}$  to  $10 \text{ nm}$ .
6. Sample holder according to any of the preceding Claims, characterised in that the film has a thickness in the range from  $0.1 \text{ }\mu\text{m}$  to  $10 \text{ }\mu\text{m}$ .
7. Sample holder according to Claim 6, characterised in that the film has a thickness in the range from  $2$  to  $4 \text{ }\mu\text{m}$ .
8. Sample holder according to Claim 7, characterised in that the film has a thickness of roughly  $3 \text{ }\mu\text{m}$ .
9. Sample holder according to any of the preceding Claims, characterised in that the substrate consists of glass or coated glass.

10. Sample holder according to Claim 9, characterised in that the glass is a conductive glass or a glass with a conductive coating.
11. Sample holder according to Claim 9 or 10, characterised in that the substrate consists of glass coated with indium tin oxide (ITO).
12. Sample holder according to any of the preceding Claims, characterised in that the porous film applied on the substrate moreover comprises:
13. Sample holder according to Claim 12, characterised in that the MALDI matrix comprises a substance selected from the group: 2,5-dihydroxy benzoic acid, 3,5-dimethoxy-4-hydroxy cinnamic acid,  $\alpha$ -cyano-4-hydroxy cinnamic acid, ferulic acid, 2,4,6-trihydroxy acetophenone.
14. Sample holder according to any of the preceding Claims, characterised in that the film applied on the substrate is present only at defined areas specifically envisaged to this end, covering same, whereas other ranges therebetween are left free of the film.
15. Sample holder according to any of the Claims 1 to 14, furthermore comprising: one or several samples to be analysed, which are applied on the film and which is or are presumed to contain one or several substances of interest.
16. Sample holder according to Claim 15, characterised in that said one or several sample(s) contain(s) substances selected from the group including nucleic acids and proteins.
17. Sample holder according to Claim 16, characterised in that the proteins are phosphorylated and/or sulphated.
18. Method of selective detection of phosphorylated/sulphated biopolymers, specifically peptides/proteins from peptide/protein mixtures, comprising the following steps of operation:

- providing a sample holder according to the present invention,
  - providing a sample which is presumed to contain phosphorylated/sulphated biopolymers, specifically peptides/proteins, alone or in combination with other biopolymers, specifically peptides/proteins, and applying the sample on the sample holder,
  - performing MALDI mass spectrometry.
19. Method of preparing a sample holder for application in MALDI mass spectrometry, with the sample holder comprising a substrate and a porous film applied on the substrate and including metal oxide particle, which method comprises the following steps of operation:
- preparing a sol from a metal oxide,
  - inducing gel formation, for example by restriction and/or thermal treatment,
  - applying the gel on a substrate,
  - drying and subsequent tempering at 200 – 600 °C, preferably 300 to 450 °C, most preferably at roughly 400 °C, for a period of 30 minutes to 180 minutes, preferably 30 minutes to 60 minutes, most preferably for roughly 45 minutes.
20. Method according to Claim 19, characterised in that the metal oxide is selected from the group including titanium dioxide, zirconium dioxide, niobium oxide, aluminium titanium oxide, tungsten zirconium oxide, hafnium dioxides, tungsten oxide, tin dioxide, lead oxide, lead dioxide, germanium dioxide and gallium oxide (TiO<sub>2</sub>, ZrO<sub>2</sub>, NbO, Al<sub>2</sub>TiO<sub>5</sub>, W<sub>2</sub>ZrO<sub>8</sub>, TiZrO<sub>4</sub>, HfO<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, PbO, PbO<sub>2</sub>, GeO<sub>2</sub> and Ga<sub>2</sub>O<sub>3</sub>).
21. Method according to any of the Claims 19 to 20, characterised in that the film has a mean pore size of < 50 nm.
22. Method according to Claim 21, characterised in that the film has a mean pore size in the range from 1 nm to 25 nm.
23. Method according to Claim 22, characterised in that the film has a mean pore size in the range from 1 nm to 10 nm.

24. Sample holder suitable for preparation according to a method according to any of the Claims 19 to 22.
25. Sample holder according to Claim 24, comprising a porous film of metal oxide particles, with the film having a mean pore size of  $< 50$  nm, preferably in the range from 1 to 25 nm, most preferably in the range from 1 nm to 10 nm.
26. Application of a sample holder according to any of the Claims 1 to 17, or any of the Claims 24 to 25 for selective detection of phosphorylated/sulphated biopolymers, specifically peptides/proteins.
27. Application according to Claim 26, with detection being performed by means of MALDI mass spectrometry.
28. Method of preparing a sample for MALDI mass spectrometry, using a sample holder according to any of the Claims 1 to 17 or any of the Claims 24 to 25, with the method comprising the following steps of operation:
  - Providing a sample holder according to any of the Claims 1 to 17 or any of the Claims 24 to 25,
  - Applying a sample on the metal oxide film of the sample holder, which is presumed to contain phosphorylated/sulphated biopolymers, specifically peptides/proteins,
  - Washing the metal oxide film in one or several washing operations,
  - Applying a phosphate-containing medium onto the metal oxide film of the sample holder,
  - applying a MALDI matrix onto the metal oxide film of the sample holder.
29. Application of the method according to Claim 28 for performing MALDI mass spectrometry.